

A NOTE ON THE CRYSTAL STRUCTURE OF SOLID H_2S .

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ABSTRACT. An attempt has been made to determine the positions of hydrogen atoms in the unit cell of solid H_2S by correlating the results of investigation of the Raman spectrum with those of the X-ray analysis of the crystal. It is pointed out that the molecule is not linear in the solid state as concluded by previous workers from results of X-ray analysis, but it is bent having the angle between the two S-H bonds equal to about 109° and the positions of the hydrogen atoms in the unit cell are exactly the same as those for the fluorine ions in the crystals of CaF_2 . The space group is O_h^2 .

The crystal structure of solid H_2S was investigated by L. Vegard¹ who concluded from the results of the study of the Debye-Scherrer patterns that the sulphur atoms are arranged in a face-centred cubic lattice, and from considerations of the symmetry of the unit cell he also came to the conclusion that the H_2S molecule is linear in the solid state. The study of the Raman spectrum of solid H_2S by the present authors,² however, revealed the fact that the H_2S molecule is not linear in the solid state but the angle between the two S-H bonds increases to about 109° in the solid state from 90° in the liquid and gaseous states. In deriving these results, the valence force system was assumed and the approximate formulæ

$$n_1^2 = \frac{f}{m} \left\{ p + (1-p) \cos^2 \alpha/2 \right\} \dots \dots \dots (1)$$

and
$$n_2^2 = \frac{f}{m} \left\{ 1 - (1-p) \cos^2 \alpha/2 \right\} \dots \dots \dots (2)$$

were used. As has been pointed out by Kohlrausch,³ since $m^2/M(M+2m)$ is small in comparison with unity, m and M being the mass of the hydrogen and sulphur atoms respectively, the above approximate formulæ can be used in the present case. The value 108° for α calculated with the help of the above formulæ is therefore not far away from the actual value. The smaller of the two fre-

quencies into which ν_1 is split up in the solid state was used in the calculations, but if the mean of these two frequencies be taken, the value of α so obtained does not differ appreciably from the tetrahedral angle. It is quite evident, therefore, that the value 180° for α obtained by Vegard from results of X-ray analysis is not correct. The purpose of the present communication is to point out that though no definite information regarding the positions of the hydrogen atoms in the unit cell can be obtained from results of X-ray analysis, such an information can be obtained by correlating the results with those of the investigation of the Raman spectrum.

According to Vegard the sulphur atoms of solid H_2S are arranged in a face-centered cubic lattice, the value of a being 5.76 A.U. and there being four molecules per unit cell. The co-ordinates of the sulphur atoms may be assumed to be 0 0 0, $0 \frac{1}{2} \frac{1}{2}$, $\frac{1}{2} 0 \frac{1}{2}$ and $\frac{1}{2} \frac{1}{2} 0$. The positions of the eight hydrogen atoms should be such that the angle α is about 109° . If the co-ordinates of the eight equivalent points in the space groups with face-centred cubic lattice be examined, only a few can give the value of α equal to about 109° . But since the molecules themselves may possess at most the symmetry C_{2v} , the symmetry of the above space groups cannot be satisfied by the four molecules when these individual molecules are taken as independent groups which are to be brought into coincidence with one another by the symmetry operations. If, however, the four sulphur atoms and eight hydrogen atoms are taken into consideration separately, the hydrogen atoms may be arranged in such a way that in each of the four molecules the S-H distance is the same as in any other molecule and also the angle α is about 109° in all the molecules. The set of co-ordinates (8 e) given in Wyckoff's Analytical Expression of the Results of Theory of Space Group can be chosen for this purpose. The arrangement of the hydrogen atoms in that case becomes the same as that of fluorine ions in the unit cell of CaF_2 . The space group then becomes O_h^5 and the co-ordinates of the hydrogen atoms are

$$\begin{array}{cccc} \frac{1}{4} \frac{1}{4} \frac{1}{4}; & \frac{1}{4} \frac{3}{4} \frac{3}{4}; & \frac{3}{4} \frac{1}{4} \frac{3}{4}; & \frac{3}{4} \frac{3}{4} \frac{1}{4}; \\ \frac{3}{4} \frac{3}{4} \frac{3}{4}; & \frac{3}{4} \frac{1}{4} \frac{1}{4}; & \frac{1}{4} \frac{3}{4} \frac{1}{4}; & \frac{1}{4} \frac{1}{4} \frac{3}{4}. \end{array}$$

The distance S-H according to the above arrangement is about 2.5 A.U., which seems to be too large, but it depends on the value of a which as found by Vegard gives for the distance between nearest sulphur atoms a value equal to 4 A.U. which seems to be a little too large.

It was mentioned in the previous communication by the present authors⁴ that the splitting up of the antisymmetric vibration ω_1 could be explained by assuming the effect of anisotropic crystalline field on this vibration and such an anisotropy might be expected in the case of a lattice other than cubic. The results of X-ray analysis were overlooked while making such a statement.

Since those results show that the lattice is a face-centred cubic one, at first sight it seems that such an anisotropic field is absent. It is possible, however, to arrange the molecules in the unit cell in such a way that during the vibration of the whole lattice, one pair of the molecules in the unit cell may be in a slightly larger crystalline field than the other. Such an arrangement is shown in figure 1. The molecules A and A' lie in planes which are at right angles to the planes of the molecules B and B'. There may be different phase relations between the vibrations of the four molecules in the lattice and thus a difference between the crystalline fields acting on the two pairs of molecules may be produced by some of these particular phase relations. For the symmetric vibration of the molecules, however, it may be seen from figure 1 that all the hydrogen atoms of the four molecules move in parallel planes and this may be the reason why there is no splitting of this vibration.

An alternative suggestion that there is only pseudo-symmetry of the hydrogen atoms and that the value of α for one pair of molecules is slightly different from that for the other pair is not tenable, because in that case the symmetric oscillation also would have been split up, but actually it is found to give a single sharp Raman line.

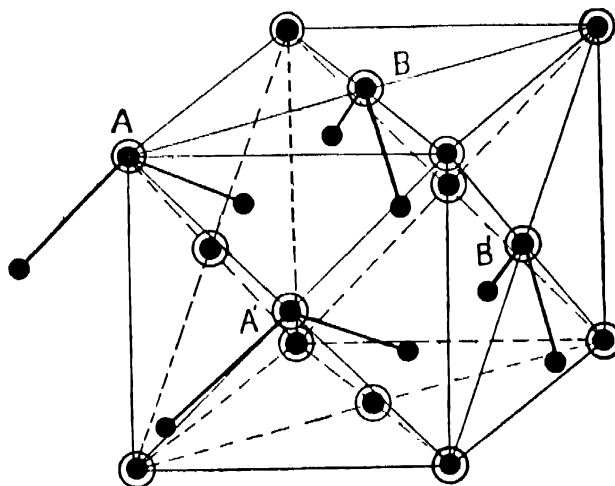


FIGURE 1.

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- ⁴ *Loc. cit.*